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PHOTOGRAPHIC PROCESS FOR THE PREPARATION OF DYE IMAGES

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Nos. 942,779, 954,308.

Numerous processes have become known for the preparation of dye images with the help of layers that change their solubility under the action of light. Such layers consist, for example, of colloids that contain dichromates or other compounds as a result of which the layers become tanned in the exposed regions.

Following the image exposure, these layers have to be treated in a solvent in order to dissolve off their unexposed parts; the layers that have been pretreated in this way are then treated with dye solutions, whereby care also has to be taken, by means special procedures, that the regions of the base that have been revealed by development are not also dyed.

It has now been found that one can significantly simplify this process for the preparation of light images with the help of layers that change their solubility under the action of light by exposing these layers to an image for sufficiently long until the exposed regions no longer take up soluble organic dyes and then dyeing the layers. In accordance with this process, the tedious procedures for dissolving off the unexposed parts of the layers and, prior to dyeing, of making the base repellent with respect to the dye are therefore avoided.

The invention is based on the knowledge that layers that change their solubility under the action of light become so strongly crosslinked and impermeable with respect to liquids as a result of sufficiently long exposure that, in addition, they are then no longer capable of swelling and are no longer capable of being dyed.

In principle, the process can be carried out with all light-sensitive substances whose sensitivity to light depends on crosslinking that is achievable by irradiation, i.e., including the dichromate-containing colloid layers that have become known up to this point in time and that are conventional on a commercial basis. Of course, not all substances that are crosslinked by light behave identically. For some, a very long exposure time is required in order to achieve the desired effect.

Often, however, the unexposed regions of the layer exposed to the image are also so readily soluble that they are dissolved out by the dye solution during the dyeing process that follows the exposure; thus one obtains absolutely no image in this case since the exposed regions no longer take on color because they have been too strongly crosslinked and the unexposed regions are no longer present. Such a case is present, for example, in conventional dichromate-containing layers. In this case, one must therefore first transform the colloid layer into a state whereby it is no longer developable, i.e., an insoluble state, by means of a uniform exposure of the whole surface, and only then does one carry out an image exposure in order to obtain a dye image by direct dyeing of the layer. A further reason that makes it difficult in such a process to use colloids that have been rendered light-sensitive by dichromate is the inherent dyeing of such layers that is always present.

Within the framework of the invention, it has been found that substances are usable that are virtually colorless in the exposed and unexposed state and whose sensitivity to light is especially high since, in this case, short exposure times are already sufficient in order to make the light-struck regions of the substance that are crosslinked by light immune with respect to dye solutions whereas the regions that have not been struck by light are still capable of being dyed without any problems.

For the implementation of the process, use is therefore made of layers with high molecular weight compounds that contain more than just one or several double bonds that are in a state of conjugation between a benzene nucleus and a carbonyl group. Such double bonds are possessed by, for example, cinnamic acid,

benzalacetophenone, cinnamalacetophenone, dibenzalacetone, furfurylideneacetophenone, cinnamalbenzalacetone and derivatives of these compounds.

Such high molecular weight compounds that contain one or several double bonds between a benzene ring and a carbonyl group in a state of conjugation (for example, in the form of chain components) can be prepared in the simplest case by reacting dioxy derivatives of the aforementioned low molecular weight compounds with, for example, dicarboxylic acids, diisocyanates or diepoxides. In this way, one obtains polycondensation compounds or polyaddition compounds in which the aforementioned groups are incorporated.

A further possibility for the preparation of soluble condensation products that have  $-C=C-CO$  groups linked to aromatic nuclei comprises the polyesterification of polyfunctional acids and alcohols whereby, by means of condensation, one incorporates cinnamic acid or its derivatives as the acid component.

The high molecular weight compounds that are usable within the framework of the invention can also carry the molecular weight groups that are being spoken about in the form of a side chain. Such compounds can be prepared in a simple manner by reacting cinnamic acid derivatives that contain at least one isocyanate group with compounds with active hydrogen atoms. In this connection, natural substances such as cellulose, starch, gelatin and their derivatives, and also synthetic materials such as polyester, polyvinyl alcohols and others can find use as such materials. One arrives at similar products if one reacts cinnamic acid derivatives with reactive hydrogen atoms with difunctional isocyanates or polyfunctional isocyanates. The

preparation of compounds of the aforementioned type is known, for example, from Austrian Patent Publication Nos. 198,256 and 198,257.

Further, high molecular weight compounds that are suitable for the process that contain more than just one or several double bonds in a state of conjugation between a benzene nucleus and a carbonyl group are the reaction products of high molecular weight compounds with unsaturated ketones that consist of two ring systems with aromatic character that are linked to one another by at least one chain and by at least one ethylene group, whereby one of the two reaction partners contains one or several groups, that carry active hydrogen atoms, whereas the other possesses one or several groups that are capable of reacting with active hydrogen. Such reactions are, for example, the subject of Austrian Patent Publication No. 197,583.

However, the range of substances that can be considered for the process in accordance with the invention is in no way limited by the data above. In this regard, it is merely essential that the compounds that are crosslinked within the framework of the process are virtually colorless and are of a sufficiently high molecular weight and are sufficiently light-sensitive, i.e., they are capable of being crosslinked by light in a short time.

One arrives at compounds that are especially active with respect to light and thus compounds that are especially suitable for the present process if one reacts benzalacetophenone derivatives, as the low molecular weight compound, with high molecular weight compounds in the form in which this is known, in particular, from Austrian Patent Publication No. 197,583. In one can, particularly easily by the selection of the rate of addition

of the two reaction partners, on one hand, prepare such a layer that, as described elsewhere, has to be developed following the image exposure, for which a small quantity of benzalaceto-phenone is adequate. On the other hand, as a result of increasing the quantity of benzalacetophenone, one is capable of preparing weakly dyed preparations that are sufficiently light-sensitive that they are so extensively crosslinked even at short exposure times that the regions that are struck by light become immune to the penetration of dye solutions. Those products that contain so much of the compound that is crosslinked by light that, depending on the choice of exposure time, they permit the use of one or the other process are, naturally, especially suitable. If one exposes the layers comprising such substances behind an original for only a very short time, approximately 5 sec, then one can prepare a negative from a positive or the converse as a result of so-called development after dissolving out the unexposed regions. If, however, instead of this, one exposes for 5 to 10 min behind a positive and does not develop, but dyes after the exposure has taken place, then one obtains a positive copy of the original that has been used.

In regard to the dyes that are usable, no general guidelines can be compiled because every dye is capable of being used that permits the substance that is crosslinked by light to be dyed in the noncrosslinked state or the merely slightly crosslinked state. Triphenylmethane, polymethine and azo dyes have proven to be especially suitable classes of dyes. Dyes that are soluble both in water and in alcohol are especially usable.

The present process is largely independent of the nature of the base, since this is not revealed during the production of the

light images. Conventional bases such as, for example, those comprising paper, metal, glass or plastics are quite generally suitable as carriers for the light-sensitive layers in accordance with the invention.

The process in accordance with the invention is suitable for the preparation of the most varied types of light images. In particular, it has significance for the preparation of copies of any desired original such as, for example, continuous tone or screen negatives or positives. Account is to be taken in this connection that the dye images that are obtained have the same brightness values as the originals, i.e., positive copies are obtained from positive originals.

It is also possible to use the light images that are obtained in accordance with the present invention for the preparation of prints in accordance with the imbibition process by, for example, removing the dye images with paper that has been moistened with alcohol. In this connection, it is even possible to repeatedly dye the light image and in this way to prepare a larger number of copies thereof. Naturally, multicolor prints can also be obtained in accordance with this process.

In addition, the process also permits the preparation of copies that are faithful in regard to color using the multilayer process. In this connection, one can proceed in such a way, for example, that one coats a completely transparent solvent-insensitive sheet, e.g., a polyester sheet, with the light-sensitive material and exposes this layer behind a yellow separation and then dyes it yellow. This yellow copy is then coated again and this second layer is exposed behind a red separation and dyed red. Finally, the red copy is again coated



and exposed behind a blue separation and then it is dyed blue. Since one now has a largely free hand in the selection of the dyes with which the individual layers are dyed - they need only to be adequately nonfading - one can select them in accordance with the colored original in question and prepare a reproduction that is faithful in regard to colors. Naturally, and in order to save time, one can also coat three sheets and expose them behind the individual color prints and dye them and then mount them in register one above the other. This works in particular when one has thin sheets at one's disposal. In approximately 10 to 15 min in this way, one can prepare a copy of a multicolor original that is faithful in regard to color.

The preparation of such direct colored copies has significance for reproduction technology and here, instead of conventional contact paper, transparencies that are faithful in regard to color can now be prepared in the shortest time in order to check for fidelity with respect to the original.

Colored graphic images, diagrams, technical drawings, etc., can also be prepared very rapidly using the process that is claimed.

#### Example 1

4.4 g polyvinyl alcohol are dissolved in 83 g formamide at approximately 100°C. 18.8 g p-isocyanatobenzalacetophenone are then stirred into this solution at 60°C and the reaction composition is then diluted with 170 g cyclohexanone. After approximately 30 min, one briefly heats to 120°C. The initially clear solution, that becomes turbid on cooling, is filtered and

the reaction product is isolated by stirring the filtrate into methanol. The light-sensitive product that is obtained is coated from a 3% cyclohexanone solution onto a completely transparent polyester foil using the centrifugal process. The light-sensitive film that is coated thereon is exposed behind the original that is to be copied for 25 to 30 sec using a 60 amp carbon arc lamp. The foil that has been exposed in this way is then dyed in a dye bath consisting of 93 parts of ethanol + 7 parts of Astraphloxin (Schultz, Dye Tables, 7th edition, No. 930), for 30 to 60 sec and then it is rinsed with water.

In order to remove the final dye fog, one treats the foil for a further 10 to 20 sec with a bath consisting of, for example, 10 g sodium bisulfite, 10 g sodium carbonate, 30 g ethanol and 50 g water and then thorough washing is carried out.

Instead of dyeing with Astraphloxin, one can also dye correspondingly with:

1. Auramine O  
Dye No. 752, Schultz, Dye Tables, 7th edition;
2. Astra red  
a condensation product made from N-ethyl-3-carbazolaldehyde and 1,3,3-dimethyl-2-methyleneindoline (Example 1, German Patent Publication No. 835,172);
3. Rhodamine 6 GDN  
Dye No. 866, Schultz, Dye Tables, 7th edition;

4. Rhodamine B  
Dye No. 864, Schultz, Dye Tables, 7th edition;
5. New fuchsin, concentrated  
Dye No. 782, Schultz, Dye Tables, 7th edition;
6. Rhoduline blue  
a condensation product made from o-chlorobenzaldehyde and  
2 mol of monoethyl-o-toluidine;
7. Victoria blue B  
Dye No. 822, Schultz, Dye Tables, 7th edition;
8. Victoria blue R  
Dye No. 821, Schultz, Dye Tables, 7th edition;
9. Methyl violet N blue  
Dye No. 783, Schultz, Dye Tables, 7th edition;
10. Crystal violet  
Dye No. 785, Schultz, Dye Tables, 7th edition;
11. Astra diamante green GX  
Dye No. 760, Schultz, Dye Tables, 7th edition;

#### Example 2

A highly filled, very well satinized baryta paper is coated, exposed, dyed and, if required, freed from dye fog as described

in Example 1. Sheets of paper can be printed from the copies that are obtained in this way by means of spirit in the spirit dampening system.

Claim

Process for the preparation of dye images using layers that change their solubility under the action of light, characterized by the feature that layers with high molecular weight compounds that contain more than just one or several double bonds in a state of conjugation between a benzene ring and a carbonyl group are exposed to an image for sufficiently long until the exposed regions do not take up soluble organic dyes and then they are dyed.